AN ASSESSMENT OF THE PREDICTIVE CAPABILITIES OF A COMPUTATIONAL MODEL FOR FUEL THERMAL STABILITY

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INTRODUCTION

The thermal stability of jet fuels is one of the major impediments facing the aerospace community in attempting to increase aircraft performance. Fuel is widely used as a coolant for critical on-board systems, and the thermal loads on the fuel resulting from this practice are steadily increasing. If this trend continues, the thermal stability limit of the fuel will soon be reached and the cooling capacity of current fuels would be exhausted. Restrictions on design parameters, particularly the maximum allowable fuel temperature, will soon be a key limiting factor in attempts to improve overall performance. Ideally, one desires a fuel which remains stable at extreme temperatures (> 1000° F), but realistically any tangible improvement in fuel stability would be welcomed. However, after decades of study, little is known of the fundamental processes leading to the deposition of solid materials on fuel system components largely due to the complexity of the processes involved, which include fuel degradation chemistry, heat transfer, and fluid mechanics.

Recent research has focused on the possibility of modeling fuel thermal stability using Computational Fluid Dynamics (CFD) with a global chemistry model. This approach allows one to examine different hypotheses about deposition mechanisms with relative speed and great flexibility. An essential element in the development of these models regards the formulation of the degradation chemistry. Typical fuels are extremely complex mixtures of hydrocarbons; therefore, attempting to model the specific reactions which contribute to deposition would be a nearly impossible chore. However, global representations of the degradation chemistry are a simple and often effective alternative to applying the full detailed chemistry.

To date, modeling efforts have focused on simulating heated tube experiments using simple, global autooxidation chemistry models[1,2]. These models have performed adequately in predicting the results of other heated tube experiments; however, their ability to predict the results of experiments with significantly different boundary conditions is questionable. Such an experiment has recently been performed at Purdue University[3] in an effort to examine the relative effects of wall and bulk fuel temperature on the deposition process. This experiment features conditions which vary greatly from those encountered in typical heated tube experiments; consequently, this experiment offers a unique vehicle with which to test and improve the current formulation of the models.

The purpose of this paper is to examine the predictive capabilities of a particular thermal stability model. This examination includes addressing the model's ability to predict the results of two basic classes of experiments: (1) constant heat flux heated tube experiments, similar to the experiments from which the model was devised and (2) constant wall temperature experiments. The results of these predictions yield valuable insights into the model's capabilities and indicate areas for possible improvement.

THERMAL STABILITY MODEL

Argonne National Laboratory/Air Force (ANL/AF) Model

The particular model applied in this study was developed by the Argonne National Laboratory in conjunction with the Air Force[1,2]. The intent of this model is to provide the capability to predict

deposition within a given fuel system component. Ultimately, related models will be employed to minimize the ill effects of fuel degradation on various fuel system components. However, it is important to note that the model is in a developmental stage and is not yet suitable for general, widespread use as a design tool.

The approach to predicting deposition with the model is based on a two-dimensional computational fluid dynamics (CFD) code. This approach offers great generality in that given the wall condition (temperature/heat flux), tube geometry, and inlet conditions (velocity and temperature) the code can predict the overall solution of the flow field including the wall and bulk fuel temperatures, pressure, radial and axial velocity components, and constituent concentrations (O_2, precursor, deposit) throughout the domain. By applying the CFD approach, the inherent coupling which exists between the chemistry, heat transfer, and fluid mechanics is preserved.

The essence of modeling fuel thermal stability lies in the degradation chemistry, which for this model is subdivided into two portions: (1) reactions occurring in the bulk fuel and (2) reactions occurring at the wall. In the bulk fuel, the following reactions apply:

$$\text{fuel} + O_2 \overset{k_1}{\rightarrow} \text{precursor} \tag{1}$$

$$\text{fuel} + \text{precursor} \overset{k_2}{\rightarrow} \text{fuel} + \text{soluble product} \tag{2}$$

where Equation 1 represents the formation of deposit precursors in the bulk fuel and Equation 2 represents the destruction of precursors at high temperatures. It is assumed that any precursor reaching the solid surface by means of diffusive and convective transport immediately forms a solid deposit on the wall. The remainder of the chemistry is a reaction at the wall whereby deposits are formed directly in the following manner:

$$\text{fuel} + O_2 \overset{k_3}{\rightarrow} \text{deposit} \tag{3}$$

The specific reaction rates for Equations 1-3 are based on Arrhenius expressions such as Equation 4 below:

$$k_n = A_n \exp\left(-E_n/RT\right) \tag{4}$$

Note that Equations 1 and 2 are based on the local *fuel* temperature while Equation 3 is based on the *wall* temperature.

After exercising the code, it becomes apparent that the deposition from the wall autooxidation reaction, represented by Equation 3, is only a small fraction of the overall deposition predicted with this model for cases where the temperature exceeds 475 K. Nonetheless, the low activation energy used for the wall autooxidation reaction ($E_3 = 8$ kcal/mole) provides a small amount of deposit on the tube walls when the wall temperature is close to room temperature. Since the bulk reactions tend to dominate the deposition process at higher temperatures, it is the bulk fuel temperature along with the dissolved oxygen concentration that are the primary drivers of fuel degradation in this code. Regarding the formation of deposits on the solid wall, which is the eventual product of the calculation, there are two mechanisms by which this occurs : (1) precursors formed in the bulk fuel (Equation 1) can reach the wall by diffusive and convective transport to form deposits and (2) deposits can be formed directly on the wall by Equation 3.

The values of the constants for the activation energies (E_n) and pre-exponential factors (A_n) were determined from experimental data[4,5,6]. These experiments, described below, consisted of flowing JP-5 over an electrically heated tube (constant heat flux) and measuring the deposition accumulated on the tube surface. The oxygen concentration at the tube inlet was taken to be the saturation value of approximately 55 ppm by weight. Values for A_n and E_n can be found in Table 1.

EXPERIMENTS MODELED

Three different experimental test cases were examined using the model described above. Two of these experiments are constant heat flux heated tube experiments which have obvious similarities. The third experiment, however, offers a challenge to the model in that the boundary conditions are quite

different than the heated tube experiments used to calibrate the model. This third experiment is a device developed at Purdue University[3] to examine the relative effects of wall and bulk fuel temperature on the observed deposition.

Heated Tube Experiments

The heated tube experiment is a widely used tool in the study of fuel thermal stability. In these experiments, fuel (initially at ambient temperature) is passed through a cylindrical metal tube which is heated by electrical resistance to thermally stress the fuel. Deposits accumulate on the tube as a result of the thermal stressing, and the deposit mass is measured to determine the degree of degradation. Some characteristics of this test are that a constant heat flux is applied to the fuel as a result of the electrical resistance heating method, and both the bulk fuel and wall temperatures increase at a roughly linear rate over the length of the tube. Data from two sets of heated tube experiments were used for model evaluations in this effort: (1) data from Marteney and Spadaccini[4,5,6] which was used to calibrate the chemical constants in the ANL/AF model, and (2) data from Giovanetti and Szetela[7,8] from similar heated tube experiments using Jet-A fuel. For both data sets the fuel was air sparged and no fuel was recirculated.

Purdue Copper Block Test

Juxtaposed against the heated tube experiments which are typical in thermal stability research, the Copper Block Test developed at Purdue[3] is markedly different. Many differences between this experiment and the heated tube experiments are clearly apparent. Chief among these differences is the manner in which the two experiments endeavor to stress the fuel. In the heated tube experiments, a constant heat flux is applied to the fuel which results in linearly increasing profiles of fuel and wall temperature along the length of the tube. The Purdue test features JP-8 flowing through a cylindrical metal tube which is embedded between two heated copper blocks. The high thermal conductivity of the copper results in a nearly constant tube wall temperature which implies a decreasing heat flux with length as bulk temperature increases. Additional features of the experiment include preheating of the fuel to temperatures (> 500 K) which are in the regime of significant fuel degradation. However, there are other subtle differences that can have a profound effect on the experimental results.

The Purdue test lacks much of the oxygen available in the heated tube experiments as the fuel is recirculated (approximately 4-5 passes through the tube in a 6 hour test) and is not air/oxygen sparged. In fact, further reduction in the fuel's oxygen content results from the practice of maintaining a N_2 overpressure on the fuel in the accumulator. Nonetheless, perhaps the most significant difference between the two experiments is the magnitude of the temperatures in the experiments. In general, the maximum temperature in the heated tube experiments is in the vicinity of 650 K, where the Purdue test reaches temperatures of 750 K. This difference in the maximum temperature could possibly account for a change in the deposition mechanism from oxidative to pyrolytic. In all, it would appear that this test bears little resemblance to the test employed to calibrate the model.

This claim is substantiated by the findings of the researchers at Purdue. In examining deposition data from their experiment against the data of Tevelde and Glickstein[9] (from another constant heat flux heated tube experiment) they found that there was a large discrepancy between the results. Figure 1 shows this discrepancy where the Purdue data appear to show the deposition rate increasing steadily with wall temperature while the Tevelde and Glickstein data clearly show the deposition rate peaking at ~ 650 K and decreasing at higher temperatures. It is our belief that a properly devised model should be able to predict both data sets accurately, and that the differences observed are merely due to the differences in the experimental methodology. Fortunately, these observed differences offer the opportunity to examine some capabilities and shortcomings of the current model formulation.

RESULTS

Predictions of Heated Tube Data

The initial task in terms of exercising the model was to calibrate the chemical constants (A_n and E_n). This was done by modeling the heated tube experiments of Marteney and Spadaccini[4,5,6] carefully tuning the chemical reaction constants (Table 1). In the calibration experiments, JP-5 fuel is driven through a long, thin long metal tube (0.237 cm ID × 2.4 m length) at a velocity of 2.1 m/s while the tube is being heated with a constant electrical power source. The high inlet fuel velocity makes the entire

flow in the tube turbulent; therefore, turbulent flow simulations have been used to predict the deposition rates under these flow conditions. Figure 2 demonstrates that the calibrated ANL/AF model does an extremely good job of representing the experimental data. In particular, the agreement between the model and the data are extremely good in the region between 500-600 K. Note the change in the slope of the curve at ~ 500 K representing the point at which the reaction in the bulk fuel begins to dominate the wall reaction. As a whole, the model is quite capable of accurately representing the data from which it was calibrated.

Figure 3 shows the model's prediction of the experiments of Giovanetti and Szetela[7,8]. One can clearly see that the model predicts the experimental data with reasonable accuracy. There is a wide scatter in the data (greater than an order of magnitude) in the region below 500 K, so it is difficult to say whether the model is representative of the data in this temperature range. However, in the region between 500-560 K, the model yields very good results and follows the sharp rise in the deposition rate. Other key features of the deposition curve are also accurately predicted; in particular, the value of the maximum deposition rate and the temperature at which it occurs are both well represented. Furthermore, the sharp decrease in the deposition rate following the peak value is also well represented by the model. The general accuracy of the model in predicting these data is encouraging, since these are not the experiments used to calibrate the model. Nonetheless, one must consider the basic similarities between the experiments modeled in Figure 3 and the experiments used to calibrate the model. All are constant heat flux heated tube experiments utilizing similar fuels (JP-5 and Jet-A) in nearly identical geometries. Quantities such as the heat flux and the mass flow rate do differ, but the experiments are exceedingly similar. Consequently, the high quality of the model predictions for these cases does not guarantee the model's predictive capabilities.

Predictions of Purdue Data

The initial calculations performed to model the Purdue experiment were done with the model in its calibrated form, and the results are provided in Figure 4. For reference, these calculations were carried out for an inlet fuel temperature of 523 K with the constant wall temperature varied between calculations. One can immediately see that the ANL/AF model fails to represent the experimental data accurately, for it overpredicts the deposition rate at low temperatures while underpredicting the deposition rate at higher temperatures. Annoyingly, the predicted deposition rate starts falling at a wall temperature of ~ 625 K whereas the experimental data indicate a monotonically increasing deposition rate with temperature. These inaccuracies in the prediction can be justified when examining some particulars of the model.

Recall that one of the differences between the calibration experiments and the Purdue experiment dealt with air sparging. While the calibration experiments were constantly supplied with fresh fuel that had been air sparged, the Purdue experiment had no mechanism to saturate the fuel with oxygen. In fact, the Purdue test configuration tends to remove oxygen from the fuel due to the N_2 overpressure on the fuel. Furthermore, since the fuel was recirculated in the Purdue test, the oxygen content in the fuel would decrease steadily with time. Therefore, one can assume that by using the saturation value of oxygen in the model that the model predictions would overemphasize the oxidative deposition in the region below 600 K. This point is clearly demonstrated in Figure 4 where the model overpredicts the deposition rate for temperatures below 600 K.

The drop in the deposition rate at higher temperatures arises from a very different aspect of the model. Recall that two reactions occur in the bulk fuel; one to form precursors in the oxidative regime and one to eliminate precursors at high temperatures. When the temperature is sufficiently high (> 650 K), the precursor destruction reaction (Equation 2) begins to dominate the precursor formation reaction. The result of this is a steadily decreasing contribution to the wall deposition rate from the reactions in the bulk fuel. Eventually, only the wall reaction contributes to the deposition, and as the oxygen is depleted this reaction will also fail to produce appreciable deposits. Therefore, the model in its calibrated form will predict little deposition at high temperatures and no deposition at very high temperatures.

These two shortcomings of the model give rise to a new approach to simulating the Purdue data. The first step being to decrease the oxygen concentration input to the model to match the low temperature deposition data, since in this region the deposition is primarily oxidative. This change is substantiated by the difference in oxygenation of the fuel between the heated tube experiments and the Purdue Copper Block Test. The second step was to derive an additional chemistry expression to simulate a non-oxidative deposition mode that functions primarily at high temperatures. Substantiation for this change arises from a belief that the deposition mechanism changes from autooxidation to pyrolysis at ~ 700 K. This reaction provides a mechanism for deposit formation when the oxidative processes are exhausted.

The results of reducing the inlet oxygen content are given in Figure 4. It was found that an inlet oxygen concentration of 10 ppm by weight (20% of the saturation value) was required to match the low temperature (~ 570 K) deposition data. The final step in the modification of the model was to devise an additional chemistry expression to simulate deposition at high temperatures. The chosen mechanism took the following form:

$$\text{fuel} \xrightarrow{k_4} \text{deposit particle} \qquad (5)$$

This reaction represents the formation of deposit particles in the bulk fuel which contribute to the wall deposition only if diffusive and convective transport carry the particles to the wall. This reaction augments the chemistry found in Equations 1-3.

Figure 5 shows the results obtained using the modified model which is a clear improvement over its unmodified counterpart shown in Figure 4. Though the results from the modified ANL/AF model are not exceptionally good, the prediction does manage to capture the essential character of the data which indicate an increasing deposition rate with increasing wall temperature. The magnitude of the deposition rate is also reasonably accurate over a large portion of the temperature range. However, one notes that the data appears to turn downward slightly at higher temperatures while the prediction clearly turns upward. This may well indicate some error in the formulation of the chemistry which is quite likely due to the extremely simple, global nature of the chemistry model.

CONCLUSIONS

The results presented here have focused on attempts to apply a computational model for thermal stability to conditions beyond those for which it was calibrated. Attempts to model experiments which were similar to the model's calibration experiment were very successful; however, deviation from the heated tube experiments to other conditions were not met with immediate success. To reasonably predict the results of the Purdue experiment, modifications to the model input and the model itself had to be made. Clearly this indicates that errors existed in the formulation of the degradation chemistry prior to its modification. Furthermore, even after modifications were made to the model with the specific purpose of better predicting the Purdue experiment, flaws were evident in the prediction.

Unfortunately, the complexity of fuel composition precludes the modeling of the individual chemical reactions leading to degradation. This point is moot, however, since these reactions are not known. The representation of the global degradation chemistry employed by the model is both extremely simple and likely in error. Experimentation is the key to making improvements to such models by pursuing a process of continually evaluating and improving the model. Ultimate success in this endeavor will lead to models which can aid in the future design of fuel system components with minimal deleterious effects from deposition.

NOMENCLATURE

A_n	pre-exponential constant	t	time
E_n	activation energy	T	temperature
k_n	rate constant	[ ]	denotes concentration
R	universal gas constant		

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TABLE 1: Constants in the Thermal Stability Model

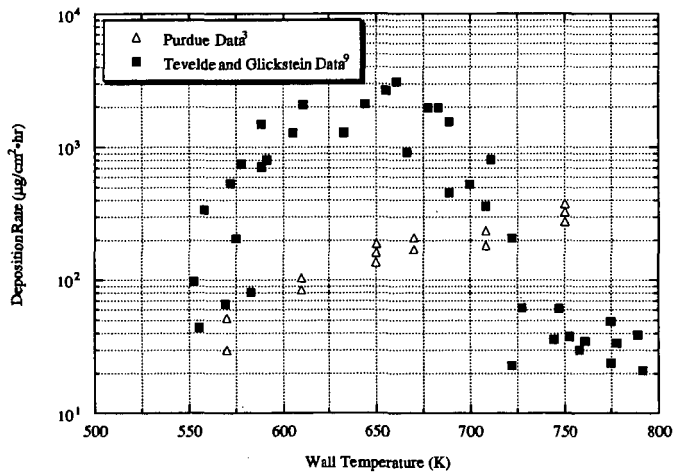| Index, n	Activation Energy, E_n (kcal/mole)	Pre-exponential Constant, A_n
1	30	1.0×10^{14} cm³/mole· s
2	35	3.0×10^{15} s⁻¹
3	8	4.0×10^{1} cm⁴/mole· s
4	40	1.0×10^{10} s⁻¹

FIGURE 1: Discrepancy in the Results of Purdue and Tevelde and Glickstein
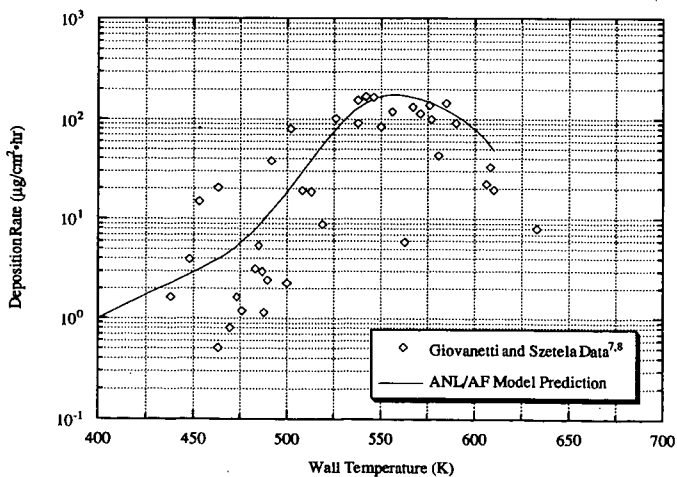
383
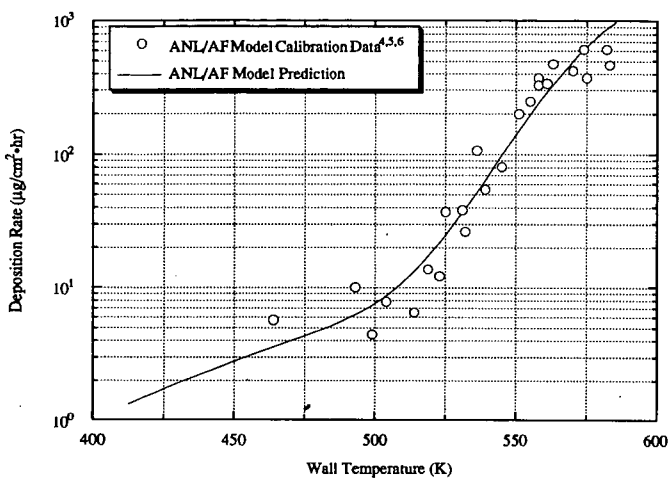
FIGURE 2: Calibration of the ANL/AF Model

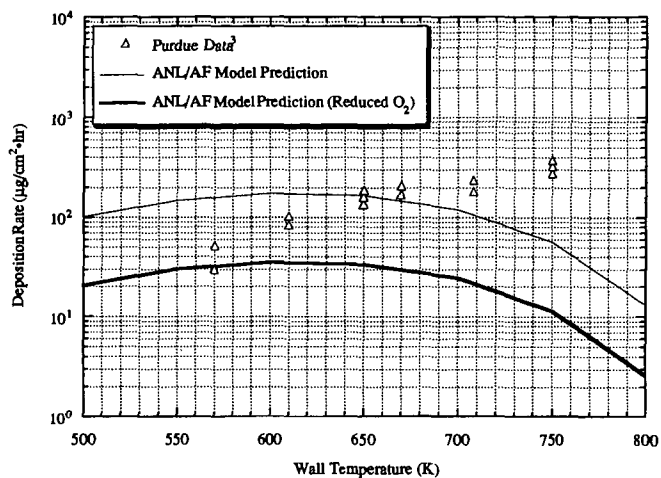FIGURE 3: Model Calculations of Heated Tube Data

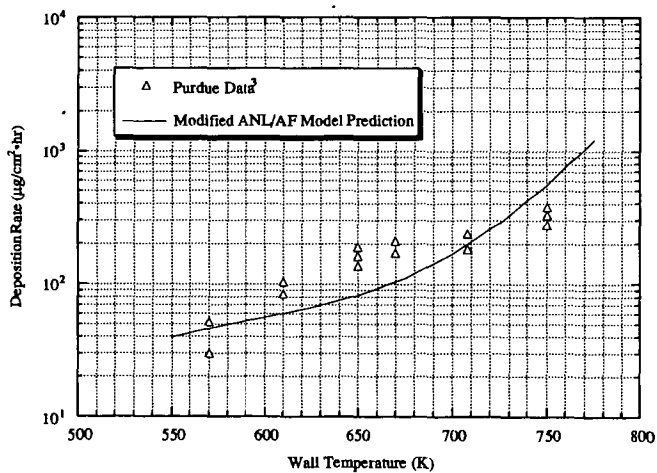FIGURE 4: Initial Attempts to Model Purdue Copper Block Test

FIGURE 5: Attempts to Predict Purdue Test with Modified Degradation Chemistry